Influence of the pulsed discharge on vibrational relaxation in aqueous sodium nitrate

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Abstract

Raman spectra of a saturated aqueous solution of sodium nitrate ($NaNO_3/H_2O$) in the region of the totally symmetric vibration $\nu_1(A)$ of the NO_3^- anion has been studied. The high-voltage pulsed electric discharge effect (HPEO activation) on the molecular relaxation in $NaNO_3/H_2O$ has been investigated. The temperature dependences of the width and frequency of the corresponding spectral line are examined.

Introduction

As is known, the high-voltage pulsed electric discharge (HPED) influences the electrochemical properties of electrolytes. Early works on this effect revealed that electric conductivity of a salt melt drastically increases alter HPED in a melt [1]. Therefore one can speak that a melt is activated by the high-voltage pulsed electric discharge (HPED) (HPED activation) and hence is in the activated stale. More recently, many works have appeared on electric conductivity studies of salt melts in strong electric fields [2]. Currently, active studies are under way to investigate HPED activation effect on the electrochemical properties of solid electrolytes [3 – 6]. Increased conductivity after HPED activation was explained by increased ion mobility in the activated stale. However, recovery of the normal value of electric conductivity is a matter of several minutes or hours and is thus an anomalously slow process. Recall that in condensed media the characteristic molecular relaxation time is of the order of 10^{-9} – 10^{-12} s. Thus we have a long-lived activated slate of a salt melt, characterized by increased ion mobility compared to the normal state of the melt at the same temperature.

Note that measurements of electric conductivity, which is a macroscopic parameter, convey averaged information about the system in general. Therefore it

makes sense to use a technique which would permit one to study the parameters and characteristics of the individual molecules or ions.

Vibrational spectroscopy allows direct measurements of molecular relaxation limes in condensed media. This method is effective in studies on salts containing molecular ions. The intramolecular vibration parameters are liable to particle (intermolecular, interionic) interactions. Therefore infrared (IR) absorption and Raman spectra are sensitive to microstructure variations of the system under study and convey information about its structural and dynamic properties [7 – 13].

It seems appealing to obtain information about the dynamic interionic interactions directly from the spectra analogous to (he phonon spectra of crystals. However, the low-frequency spectrum of ionic melts and high-temperature phases of ionic crystals is generally a wide structureless band. Al the same lime, structural and dynamic changes in a salt system affect the vibrational slates of the structural units of the system and are reflected on the Raman and 1R absorption spectra. Therefore using the vibrational spectra corresponding to the inner modes of molecular ions to derive information about molecular relaxation in ionic crystals and melts seems to be quite justified.

Previously, we found that HPED influences the vibrational spectra and the wing of the Rayleigh scattering line in melted [14, 15], crystal [16], and heterogeneous [17] salt systems. Note that spectrum recording lime is several minutes, i.e., much longer than the characteristic time of molecular relaxation in condensed media. Nevertheless, we recorded changes in the vibrational bands and the wing of the Rayleigh scattering line in the activated slates of salt systems [14 – 17] compared to the nonactivated states.

Thus it may be staled that the long time of HPED aftereffect on the electrochemical and spectral properties of alkaline metal chlorides, nitrates, nitrites, thiocyanates, acetates, and sulfates is a challenge in the chemical physics of salt systems.

Investigation of the HFED effect on the vibrational spectra of ionic solutions is a natural continuation of our works. Variations in the density, viscosity, electric and heal conduction of alkali salt solutions were studied in [18 – 21]. The aim of this work is to study the effect of HPHD activation on the Raman spectra of saturated aqueous sodium nitrate.

Experiment

The Raman spectra were recorded on a DFS-24 spectrometer using the standard 90° procedure [22] (monochromator I/O slit width 100-200 μm). The corresponding optical slit width was 1.7 – 3.4 cm^{-1}. The Raman spectra were excited with an argon laser LGN-503. A laser line with λ=488 nm was used. A laser beam passed through a Glenn-Thomson prism and then through an optical filter not transmitting radiation with λ>488 nm; then it was focused on a cell with a solution.

Solutions were prepared using distilled water and sodium nitrate of chempure grade (99.8%). The Raman spectra of $NaNO_3/H_2O$ were measured in the range of the totally symmetric vibration $\nu_1(A)\approx1050$ cm^{-1} of the nitrate ion NO_3^-. The spectral interval under analysis was 1000–1100 cm^{-1}. The recording lime was 5.5 min per spectrum. The analysis was performed in the temperature range 18 – 90°C. The temperature of the solution was kept constant with a high-precision temperature regulator VRT-2 to an accuracy of ±1°C and measured with a calibrated chromel-alumel thermocouple. The accuracy of determination is ±0.5 cm^{-1} for the position of maximum *v* of the vibration band and ±0.1 cm^{-1} for the bandwidth δ.

To analyze the HPED activation effect on the spectral properties of the solutions we employed a high-voltage pulsed arrester [14]. Output voltage on the arrester may be adjusted at values from 3.3 to 7.8 kV. The basic working capacitor of the arrester (K.BG-II, 0.1 μF, 15 kV) is discharged through two platinum electrodes, submerged in the cell with the solution. The distance between electrodes in solution is several millimeters. As a result of the discharge of the working capacitor, a pulsed discharge passes through the solution. The volume of the solution is approximately 1 ml.

Results and discussion

Figure 1 shows the dependence of the width of the vibration band δ on the time *t*. The first five points were obtained without applying an electric field. Then a discharge was passed through the solution. The discharge voltage was 7.8 kV. The Raman spectrum was recorded immediately alter the discharge. HPED leads to narrowing of he spectral band width. After the discharge, the total background of scattering increases. Subsequently, the initial δ value and the total background are restored. An analogous picture was observed every time when HPED activation was performed.

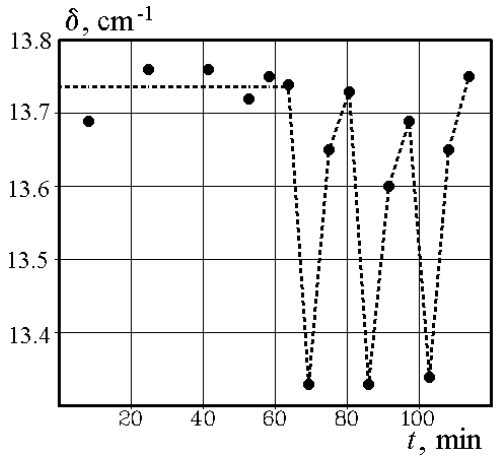

Figure 1. Effect of a pulsed electric discharge on the contour width in the Raman spectrum corresponding to the ν_1(A) vibration of NO_3^- in a saturated aqueous solution of sodium nitrate.

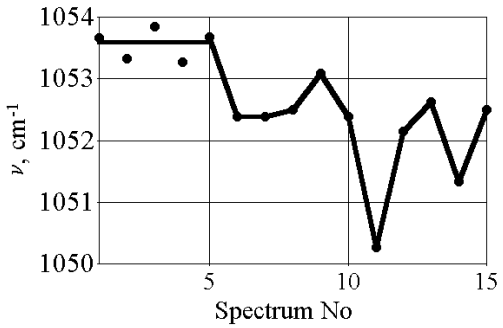

Figure 2. Effect of a pulsed electric discharge on the position of the contour maximum in the Raman spectrum corresponding to the ν_1(A) vibration of NO_3^- in a saturated aqueous solution of sodium nitrate.

The band width δ is inversely proportional to the relaxation time τ of the vibrationally excited states of molecules:

$$\tau = \frac{1}{\pi \cdot c \cdot \delta}. \quad (1)$$

A decrease in the band width as a result of HPED activation indicates that the rate of molecular relaxation in the activated state of the solution decreases compared to the normal stale.

The maximum ν of the vibration band is also shifted after HPED (Figure 2). In Figure 2 spectrum numbers are plotted on the horizontal axis. The scale along the abscissa axis is absolutely identical to the corresponding lime scale in Figure 1. The time interval between the spectra is 5.5 min. The first five points correspond to the nonactivated state. In the activated stale the ν value decreases and then gradually returns to its initial value.

Figures 3 and 4 present the temperature dependences of the width δ(*T*) and maximum position ν(*T*) of the vibration band. Both δ and ν decrease oppositely with temperature. Thus HPED activation is analogous, to some extent, to a temperature

increase by several dozens of degrees. The discharge energy suffices to heat the solution by only 1.5°C. Changes in spectral parameters were also observed in studies on HPED effect on the spectra of melts. In melted salts, the band width increases with temperature [22 – 26], as it does in the activated stale of the melt compared to the nonactivated state [14, 15]. Again, the observed spectral changes may not be explained by melt healing due lo discharge energy.

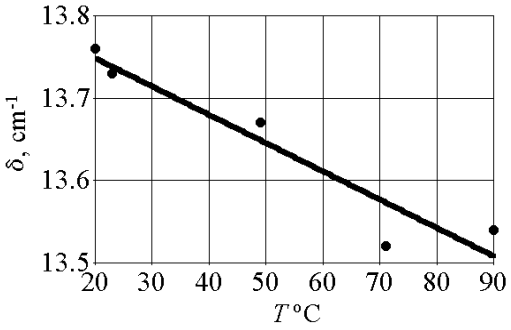

Figure 3. Temperature dependence of the contour width in the Raman spectrum corresponding to the ν_1(A) vibration of NO_3^- in a saturated aqueous solution of sodium nitrate.

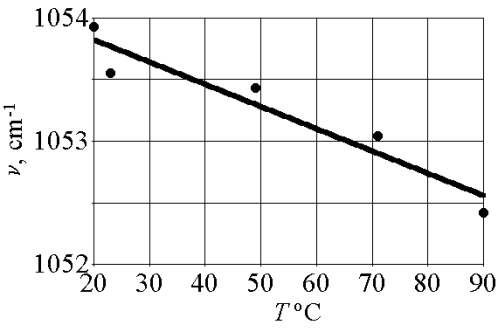

Figure 4. Temperature dependence of the position of the contour maximum in the Raman spectrum corresponding to the ν_1(A) vibration of NO_3^- in a saturated aqueous solution of sodium nitrate.

For more profound understanding of reasons for ihe slower molecular relaxation in the activated stale of the solution, one must consider in more detail the relaxation processes which may occur in this system. As is known, molecular relaxation may be vibrational or orientational. Vibrational relaxation processes are further grouped into adiabatic and nonadiabatic. Among adiabatic processes, vibrational dephasing is of greatest importance. Nonadiabatic processes are relaxation processes due to repulsive, dipole-dipole, and ion-dipole interactions, as well as resonance exchange of vibrational quanta and intramolecular decay of the vibrational states. Therefore the band width may be represented as the sum of the corresponding terms [23]:

$$\delta = \delta_{vd} + \delta_{dd} + \delta_{id} + \delta_{rep} + \delta_{res} + \delta_{int} + \delta_{or}. \quad (2)$$

Here δ_{vd} is the vibrational dephasing term; δ_{dd}, δ_{id} and δ_{rep} are the dipole-dipole, ion-dipole, and repulsive terms; δ_{res} is the contribution resulting from the resonance transmission of vibrational quanta; δ_{int} is the contribution from the intramolecular decay

of the vibrationally excited stales; δ_{or}, is the orientational relaxation term.

Let us analyze formula (2) with regard to the Raman spectra in the region of $\nu_1(A)$ of the NO_3^- anion in $NaNO_3/H_2O$. The $\nu_1(A)$ line is strongly polarized (depolarizalion is 0.06) [27]. Therefore NO_3^- reorientation does not directly contribute to the δ value in the isotropic Raman spectrum: $\delta_{or}=0$. The probability of the resonance transmission of the vibrational quanta is also small ($\delta_{res}=0$), since the nearest neighbors of the nitrate ion in solution are Na^+ cations, but not the identical anions. We can also ignore the contribution from the intramolecular decay of the vibrationally excited stales ($\delta_{int}=0$) because the difference between $\nu_1(A)$ and the nearest intramolecular vibration $\nu_2(A)\approx 810$ cm^{-1} of the nitrate ion is of the order of 250 cm^{-1}. Therefore the decay of ν_1 with further excitation of ν_2 demands dissipation of a large amount of energy to translational degrees of freedom, but this is unlikely to occur. Ion-dipole and dipole-dipole interactions can be realized for the nitrate ion in solution because the NO_3^- anion is distorted and acquires a nonzero dipole moment in solution [28]. Note that the ion-dipole interactions of the nitrate ion are with the Na^+ cations, and the dipole-dipole interactions, with the water molecules. Since the ion-dipole interactions are stronger, their contribution to the band width is greater compared to the dipole-dipole interactions. The $\nu_1(A)$ line also has broadenings due to repulsive interactions and vibrational dephasing processes, which are universal.

Now the band width is recorded as

$$\delta = \delta_{vd} + \delta_{dd} + \delta_{id} + \delta_{rep}. \quad (3)$$

Vibrational relaxation processes are generally more intense at elevated temperatures. This lakes place in melts [22-26]. In solution, however, δ decreases at elevated temperatures. To analyze changes in the terms of formula (3) under the action of various factors such as temperature variation and HPHD activation, we must adopt a certain structural model for solution. In our opinion, a salt system (solution or melt) consists of ion-associated complexes (IAC) [22-26]. One can assume that at elevated temperatures the solution structure is more homogeneous, and partial destruction and rearrangement of IAC take place. Among the nearest neighbors of the nitrate ion, the content of the water molecules increases, and that of the Na^+ cations decreases. The terms δ_{dd} and δ_{id} change accordingly. However, the latter contribution is greater than the

former and hence the effect of the decreased δ_{id} on δ is more significant than that of the increased δ_{dd}. As a result, δ decreases at elevated temperatures. In a melt, the Na^+ cations are the nearest neighbors of the nitrate ions irrespective of the temperature. Therefore δ increases with the temperature of the melt because all terms of Eq. (3) increase [22-26].

Analogous reasoning may be given in respect of HPED activation. As a result of a discharge induced by a powerful water hammer, IAC may undergo partial destruction and rearrangement. The rate of vibrational relaxation increases or decreases depending on the character of IAC rearrangement. The experimentally observed decrease in δ indicates that HPED activation as well as temperature elevation leads to a higher content of water molecules and a lower content of Na^+ cations among the nearest neighbors of the nitrate ion. These changes can decrease the ion-dipole term. In our previous investigations on HPED effect on the vibrational spectra of salt melts, δ generally decreased after discharge [14, 15]. In a melt, the cations are generally the nearest neighbors of the anions. This holds for both the normal and activated slate of the melt. At the same time, HPED activation and partial destruction of IAC considerably increase the rate of phase relaxation, and are thus the reasons for the increased width of vibration bands in melts.

Note that the lower content of the Na^+ cations and the higher content of the water molecules among the nearest neighbors of the nitrate ion as a result of HPED activation in $NaNO_3/H_2O$ may lead to lower rates of vibrational dephasing. This circumstance also narrows the $\nu_1(A)$ hand when the solution passes to the activated state. Analogous factors may decrease the δ value at elevated temperatures.

Conclusions

Activation of a sail system (ionic crystal, melt, solution) by a high-voltage pulsed electric discharge leads to the activated stale of the system corresponding lo system healing by several degrees. The real temperature of the system in this case is practically invariable. Hence it follows that the activated state of a salt system is a long-lived, strongly nonequilibrium slate. It is characterized by the greater homogeneity of the microstructure and the greater ion mobility compared to the nonactivated state.

After the discharge, the salt system gradually returns lo its normal stale. However,

the recovery time is several minutes. This has not yet been explained in terms of the existing concepts and remains one of the challenges in the chemical physics of salt systems.

Acknowledgments

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References

1. O.M. Shabanov, S.M. Gadzhiev, S.M. Tagirov, Rus. J. Electrochem., 9 (1973) 1828.
2. S.M. Gadzhiev, V.D. Prisyazhnyi, in: Ionic Melts and Solid Electrolytes, Naukova Dumka, Kiev, 1986, p. 21.
3. S.M. Gadzhiev, R.M. Guseinov, V.D. Prisyazhnyi, Ukrainian Chem. J. 57 (1991) 47.
4. R.M. Guseinov. S.M. Gadzhiev, V.D. Prisyazhnyi, Melts, (5) (1991) 91.
5. R.M. Guseinov, S.M. Gadzhiev, Z.G. Gebekova, Rus. J. Electrochem., 33 (1997) 1295.
6. S.M. Gadzhiev, R.M. Guseinov, Z.G. Gebekova, A.S. Gadzhiev, Rus. J. Electrochem., 34 (1998) 106.
7. S.A. Kirillov, Chem. Phys. Report, 11 (1992) 678.
8. I.S. Perelygin, J. Struct. Chem. 38 (1997) 270.
9. S.A. Kirillov, I.S. Musienko, Chem. Phys. Report, 16 (1997) 30.
10. M.M. Gafurov, A.R. Aliev, Spectrochim. Acta, 55A (1999) 1237.
11. M.M. Gafurov, A.R. Aliev, I.R. Akhmedov, Spectrochim. Acta, 58A (2002) 2683.
12. A.R. Aliev, M.M. Gafurov, I.R. Akhmedov, Chem. Phys. Lett. 359 (2002) 262.
13. A.R. Aliev, M.M. Gafurov, I.R. Akhmedov, Mol. Phys. 100 (2002) 3385.
14. A.R. Aliev, M.M. Gafurov, Melts, (1) (1992) 30.
15. M.M. Gafurov, A.R. Aliev, V.D. Prisyazhnyi, Ukrainian Chem. J. 58 (1992) 711.
16. A.R. Aliev, M.M. Gafurov, I.R. Akhmedov, Chem. Phys. Lett. 353 (2002) 270.
17. M.M. Gafurov, V.D. Prisyazhnyi, A.R. Aliev, Ukrainian Chem. J. 59 (1993) 1015.

18. P.C. Su, I.N. Maksimova, Ukrainian Chem. J. 50 (1984) 579.
19. P.C. Su, I.N. Maksimova, Rus. J. Appl. Chem. 58 (1985) 491.
20. P.C. Su, I.N. Maksimova, Rus. J. Phys. Chem. 59 (1985) 1265.
21. U.B. Magomedov, High Temperatures, 36 (1998) 48.
22. M.M. Gafurov, I.R. Akhmedov, A.R. Aliev, J. Appl. Spectrosc. 52 (1990) 429.
23. M.M. Gafurov, A.R. Aliev, A.Z. Gadzhiev, Melts, (1) (1989) 111.
24. M.M. Gafurov, V.D. Prisyazhnyi, A.R. Aliev, Ukrainian Chem. J. 56 (1990) 1244.
25. A.R. Aliev, A.Z. Gadzhiev, J. Appl. Spectrosc. 59 (1993) 465.
26. M.M. Gafurov, A.R. Aliev, Melts, (3) (1997) 35.
27. T. Kato. J. Umemura, T. Takenaka, Mol. Phys. 36 (1978) 621.
28. G.A. Krestov, N.P. Novoselov, I.S. Perelygin, et al., Ion Solvation, Nauka, Moscow, 1987, p. 122.